



(19)  European Patent Office
Office européen des brevets

A standard linear barcode is positioned horizontally across the page, consisting of vertical black bars of varying widths on a white background.

(11) EP 0 601 881 B1

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:
22.04.1998 Bulletin 1998/17

(51) Int. Cl.⁶: **B29D 9/00**, B29C 45/16,
C08J 5/12, C08L 83/04
// B29K23/00, B29K83/00

(21) Application number: 93309992.1

(22) Date of filing: 10.12.1993

(54) Polypropylene resin/silicone rubber Integrally molded article and method for making

Einstückig geformter Gegenstand aus Polypropylen und Siliconkautschuk und dessen Herstellungsverfahren

Article moulé intégralement en polypropylène et caoutchouc de silicium et procédé pour le fabriquer

(84) Designated Contracting States:
DE FR GB

- Shimamoto, Noboru
Annaka-shi, Gunma-ken (JP)
- Yamamoto, Yasushi
Takasaki-shi, Gunma-ken (JP)
- Kuchiki, Eiji
Kawagoe-shi, Saitama-ken (JP)
- Fujita, Yuji
Tokorozawa-shi, Saitama-ken (JP)

(30) Priority: 10.12.1992 JP 352677/92
10.12.1992 JP 352678/92

(43) Date of publication of application:
15.06.1994 Bulletin 1994/24

(73) Proprietor:
SHIN-ETSU CHEMICAL CO., LTD.
Chiyoda-ku Tokyo (JP)

(74) Representative:
Stoner, Gerard Patrick et al
MEWBURN ELLIS
York House
23 Kingsway
London WC2B 6HP (GB)

(72) Inventors:

- Shudo, Shigeki
Annaka-shi, Gunma-ken (JP)
- Fujiki, Hironao
Takasaki-shi, Gunma-ken (JP)
- Matsuda, Akira
Annaka-shi, Gunma-ken (JP)

(56) References cited:

EP-A-0 143 994

US-A-4 257

EEP0601881B1

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

Description

This invention relates to integrally moulded articles of polypropylene resin and silicone rubber, useful in the areas of electric equipment, electronic equipment, automobiles, precision machines and the like, and to methods for preparing the same.

A number of methods have been proposed for providing a bond between addition curing type silicone rubber and organic resins. It is known, for example, to form a bond by applying a primer to a surface of moulded resin, applying uncured silicone rubber material thereto and curing the silicone rubber to the resin, or by curing a self-adhesive silicone rubber composition directly onto moulded resin. For self-adhesive silicone rubber compositions, a number of proposals have been made for their tackifier component.

As another approach, it is known from EP-A-143994 to add an organohydrogenpolysiloxane containing at least 30 mol% of hydrogen atoms directly attached to silicon atoms to an organic resin so that the resin is bondable with addition curing type silicone rubber. The resin may be polypropylene. It is also suggested to add unsaturated resin to the organic resin to improve bonding. JP-B 45292/1988 discloses integration by physically fitting silicone rubber within moulded organic resin. In JP-A-193843/1988, a compound having an aliphatic unsaturated group and a hydrolysable group attached to a silicon atom is grafted to an olefin resin and silicone rubber is bonded and integrated with the grafted olefin resin. Furthermore, as we previously proposed in EP-A-540259, a thermoplastic resin can be bonded and integrated to a silicone rubber composition when a compound having an unsaturated group and a hydrogen atom directly attached to a silicon atom is added to the resin.

However, several problems arise with these prior art methods for integrating silicone rubber and organic resin into a one-piece article. The primer method is cumbersome in that the initially-moulded resin shape must be taken out of the mould before the primer can be applied thereto.

Where a self-adhesive addition curing type silicone rubber material is applied and cured to a resin preform, the resulting bond strength is insufficient for use as a one-piece member if the resin is a polypropylene resin.

Where organohydrogenpolysiloxane is added to olefin resin, the properties of the resin itself can be altered thereby, preventing the resin from exerting its own properties. The physical engagement method leaves the possibility that the two segments may be disengaged by physical forces. The known use of an olefin resin having grafted thereto a compound having an aliphatic unsaturated group and a hydrolysable group attached to a silicon atom cannot obviate the use of primer when joining to addition curing type silicone rubber.

Silicone rubber has found a spreading use in the fields of electric and electronic equipment and automobiles because it is recognized as highly reliable in heat resistance, weatherability and electrical properties. There is a corresponding demand for integral mouldings in which thermosetting resin, especially polypropylene resin, and silicone rubber are firmly united or bonded together.

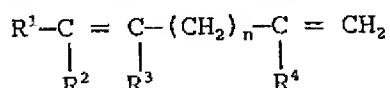
An object of the present invention is to provide a polypropylene resin/silicone rubber integrally moulded article wherein the polypropylene resin and the silicone rubber are joined at a practically acceptable bond strength. Another object is to provide a method for preparing such a polypropylene resin/silicone rubber integrally moulded article in a simple reliable manner within a short time, typically by an injection moulding technique.

We have found that an integrally moulded article in which silicone rubber and polypropylene resin are joined at a practically acceptable bond strength using a specific modified polypropylene and addition-curing silicone.

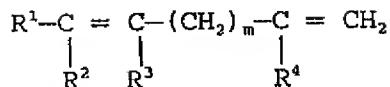
Specifically, a first aspect of the invention is a polypropylene/silicone rubber integrally moulded article in which

(a) a polypropylene component made of polypropylene resin selected from

(i) random copolymers of propylene with non-conjugated diene of the formula



where groups R¹ to R⁴ are selected independently from H and C₁₋₆ alkyl, and n is an integer in the range from 1 to 20, and (ii) graft copolymers of polypropylene graft-polymerised with non-conjugated diene of the formula



5

where groups R^1 to R^4 are selected independently from H and C_{1-6} alkyl, and m is an integer in the range from 1 to 20;

10 or of a resin composition containing such a polypropylene resin, is integrally joined to
 (b) an addition-type silicone rubber obtainable from a composition comprising

15 (i) alkenyl group-containing organopolysiloxane;
 (ii) organohydrogenpolysiloxane having per molecule at least two hydrogen atoms directly attached to silicon atom, and
 (iii) addition reaction catalyst.

A second aspect is a method of making such an article in which the polypropylene component is moulded to a pre-form, the addition-curable silicone rubber composition is contacted with a surface of the preform and cured at a temperature below the polypropylene component's softening temperature.

20 Stronger bonding is established when the silicone rubber composition contains a tackifier component selected from (I) compounds containing in a molecule at least one hydrogen atom directly attached to a silicon atom and at least one of an alkoxy silyl group, glycidyl group and acid anhydride group, and (II) compounds containing in a molecule at least one hydrogen atom directly attached to a silicon atom and a divalent linkage $-(CR^1R^2)_n-$ wherein each of R^1 and R^2 is 25 a hydrogen atom or a substituted or unsubstituted monovalent hydrocarbon group having 1 to 10 carbon atoms and n is an integer of from 2 to 30. Particularly when the silicone rubber composition contains compound (II), it may be moulded over the polypropylene resin by an injection moulding technique and cured thereto within a short time to provide a firm bond. At the same time, the silicone rubber itself is releasable from the mould in a practically acceptable manner.

30 Preferably both the moulding and contacting steps of the method are done by injection moulding.

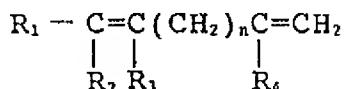
BRIEF DESCRIPTION OF THE DRAWINGS

FIGS. 1A and 1B are side and plan views of an adhesion test piece;
 35 FIG. 2 is a schematic cross-sectional view of an injection moulding machine used in preparing a moulded article;
 FIG. 3 is a schematic cross-sectional view similar to FIG. 2 at a stage when a polypropylene resin is injection moulded;
 FIG. 4 is a schematic cross-sectional view similar to FIG. 2 at a stage when a left mould half is reversed;
 40 FIG. 5 is a schematic cross-sectional view similar to FIG. 2 at a stage when a silicone rubber composition is injection moulded, and
 FIG. 6 is a perspective view of a moulded article obtained from the stage of FIG. 5.

A polypropylene resin having an aliphatic unsaturated group is used herein. The term polypropylene resin encompasses resins including a propylene unit. More particularly, the polypropylene resins are classified into two classes (I) and (II) as described below. Random copolymers of propylene with a diene having the structure $CH=C(CH_3)_2$ are disfavoured because they are less adhesive.

45 Class (I) includes random copolymers of propylene with a non-conjugated diene compound of the following general formula.

50



55

In the formula, R_1 to R_4 are independently hydrogen atom or alkyl group having 1 to 6 carbon atoms. It is preferred

that R₁ and R₂ are not both methyl groups when R₃ is a hydrogen atom, n is an integer of 1 to 20.

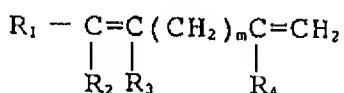
Exemplary of the non-conjugated diene are 2-methyl-1,4-pentadiene, 1,4-hexadiene, 4-methyl-1,4-hexadiene, 1,4-heptadiene, 4-methyl-1,4-heptadiene, 4-ethyl-1,4-heptadiene, 1,5-heptadiene, 1,5-octadiene, 5-methyl-1,5-heptadiene, 2-methyl-1,5-hexadiene, 1,6-octadiene, 6-methyl-1,6-octadiene, 2-methyl-1,6-heptadiene, 1,9-decadiene, and 1,13-tetradecadiene. Also useful are cyclic non-conjugated dienes such as vinylcyclohexene, vinylnorbornene, dicyclopentadiene, and ethyldenenorbornene, and trienes such as 1,3,7-octatriene and 1,5,9-decatriene. Preferred among these are 1,9-decadiene and 1,13-tetradecadiene. These non-conjugated diene compounds may be used alone or in admixture of two or more.

Random copolymerization of propylene with the non-conjugated diene compound may be effected by, for example, conventional copolymerization methods using Ziegler-Natta catalysts. Preferably the non-conjugated diene is used in an amount of about 0.01 to 20 mol%, more preferably about 0.05 to 15 mol%, most preferably about 0.1 to 10 mol% of the copolymer. Weaker bonding force would be exerted between copolymers with a non-conjugated diene content of less than 0.01 mol% and the silicone rubber. Copolymers with a non-conjugated diene content of more than 20 mol% would suffer from some loss of crystallinity.

Another unsaturated compound such as ethylene and butene-1 may be copolymerized with the random copolymers.

The copolymers generally have a melt flow rate (MFR) of 0.01 to 1,000 g/10 min. at a temperature of 230°C under a load of 2.16 kg. It is also acceptable to blend the random copolymer with a different type of polyolefin.

Class (ii) includes graft copolymers in which polypropylene is graft polymerized with a diene compound of the following general formula.



25

In the formula, R₁ to R₄ are independently hydrogen atom or alkyl group having 1 to 6 carbon atoms and m is an integer of 1 to 20.

Exemplary of the diene are 2-methyl-1,4-pentadiene, 1,4-hexadiene, 4-methyl-1,4-hexadiene, 4-methyl-1,4-heptadiene, 4-ethyl-1,4-heptadiene, 1,5-heptadiene, 1,5-octadiene, 5-methyl-1,5-heptadiene, 2-methyl-1,5-hexadiene, 1,6-octadiene, 6-methyl-1,6-octadiene, 2-methyl-1,6-heptadiene, 1,9-decadiene, and 1,13-tetradecadiene. Also useful are cyclic non-conjugated dienes such as vinylcyclohexene, vinylnorbornene, dicyclopentadiene, and ethyldenenorbornene, and trienes such as 1,3,7-octatriene and 1,5,9-decatriene. Preferred among these are 1,9-decadiene and 1,13-tetradecadiene. These non-conjugated diene compounds may be used alone or in admixture of two or more.

A diene is grafted to polypropylene by radical polymerization using any desired method, for example, a solution method of dissolving polypropylene in an organic solvent such as xylene and toluene and adding a diene and a radical generating agent to the solution for reaction to take place, or a melt milling method of melting and milling a mixture of polypropylene, diene and radical generating agent in an extruder for reaction to take place. Preferably the diene is used in an amount of about 0.01 to 20 mol% of the resulting copolymer.

Preferred examples of the radical generating agent or reaction initiator include peroxides such as benzoyl peroxide, lauroyl peroxide, di-tert-butyl peroxide, acetyl peroxide, tert-butyl peroxyvalate, 2,5-dimethyl-2,5-di-tert-butyl peroxyhexine, and tert-butyl peroxybenzoate, and diazo compounds such as azobisisobutyronitrile. The radical generating agent is desirably used in an amount of about 1 to 50 parts by weight per 100 parts by weight of the monomer having an unsaturated bond. The graft copolymer generally has an MFR of 0.01 to 1,000 g/10 min. It is also acceptable to blend the graft copolymer with a different type of polyolefin.

A different e.g. conventional polypropylene may be blended with the modified polypropylenes (i) and (ii) described above.

50 The silicone rubber to be integrally joined with the above-defined polypropylene resin or a composition containing the same is an addition cured silicone rubber. Preferably the silicone rubber is obtained by curing a silicone rubber composition comprising (a) an alkenyl group-containing organopolysiloxane, (b) an organohydrogenpolysiloxane having at least two hydrogen atoms each directly attached to a silicon atom in a molecule, and (c) an addition reaction catalyst.

Component (a) is an organopolysiloxane containing an alkenyl group which may be selected from well-known organopolysiloxanes conventionally used as a major component of addition curing type silicone rubber compositions, typically having a viscosity of about 100 to 100,000 centipoise at room temperature.

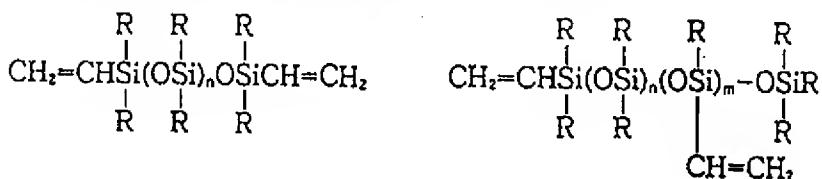
Preferred organopolysiloxanes are represented by the general formula: R_aSiO_{(4-a)/2} wherein R is a substituted or unsubstituted monovalent hydrocarbon group, preferably having 1 to 8 carbon atoms. Examples of the hydrocarbon

group represented by R include alkyl groups such as methyl, ethyl and propyl; alkenyl groups such as vinyl, propenyl and butenyl; aryl groups such as phenyl and xylyl; and halo- or cyano-substituted hydrocarbon groups such as 3,3,3-trifluoropropyl. The monovalent hydrocarbon groups may be identical or different as long as an alkenyl group is contained in the organopolysiloxane molecule. The content of alkenyl group is preferably 0.01 to 10 mol%, especially 0.1 to 1 mol% of the entire R groups. Letter a is a number of 1.9 to 2.4. The organopolysiloxane may be a linear one or a branched one further containing a $\text{RSiO}_{3/2}$ unit or $\text{SiO}_{4/2}$ unit. The substituent on the silicon atom is basically any of the above-mentioned groups. It is desirable to introduce a vinyl group among the alkenyl groups and a methyl or phenyl group among other substituent groups.

Illustrative, non-limiting examples of the organopolysiloxane are given below.

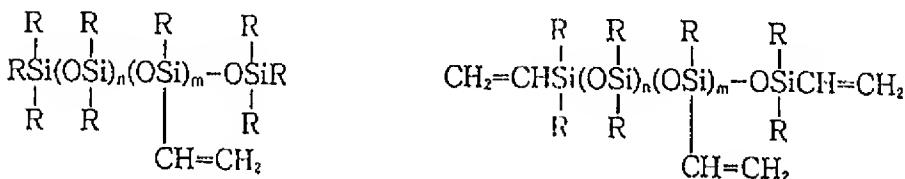
10

15



20

25



30 In these formulae, R is as defined above (excluding an aliphatic unsaturated group), and letters m and n are positive numbers meeting $m + n = 100$ to 5000 and $m/(m + n) = 0.001$ to 0.1.

The organopolysiloxanes may be prepared by per se known methods. For example, they are obtained by effecting equilibration reaction between an organocyclopolsiloxane and a hexaorganodisiloxane in the presence of an alkali or acid catalyst.

35 Component (b) is an organohydrogenpolysiloxane which serves as a cross linking agent by reacting with component (a). It is not particularly limited in molecular structure and may be any of conventionally used organohydrogenpolysiloxanes of linear, cyclic and branched structures. However, it should have at least two hydrogen atoms each directly attached to a silicon atom in a molecule. The substituent or substituents attached to a silicon atom other than hydrogen are the same as the substituents described for organopolysiloxane (a).

40 Component (b) is preferably added in an amount to provide 0.4 to 5 equivalents, especially 0.8 to 2 equivalents per alkenyl group in component (a). Less than 0.4 equivalents of component (b) on this basis can result in cured silicone rubber having a too low crosslinking density and hence, less heat resistance. More than 5 equivalents of component (b) sometimes gives rise to a bubbling problem due to dehydrogenation reaction, also adversely affecting heat resistance.

The organohydrogenpolysiloxanes may be prepared by per se known methods. For example, the most commonly used method is by equilibrating octamethylcyclotetrasiloxane and/or tetramethylcyclotetrasiloxane and a compound containing a hexamethyldisiloxane or 1,1-dihydro-2,2,3,3-tetramethyldisiloxane unit which will become a terminal group in the presence of a catalyst such as sulfuric acid, trifluoromethanesulfonic acid, and methanesulfonic acid at a temperature between -10°C and +40°C.

45 Component (c) is an addition reaction catalyst which is generally selected from platinum and platinum compounds. Since the catalyst is used for promoting curing addition reaction or hydrosilation between components (a) and (b), it may be, for example, a conventional known one. Exemplary are platinum black, chloroplatinic acid, alcohol modified chloroplatinic acid, complexes of chloroplatinic acid with olefins, aldehydes, vinylsiloxanes or acetylene alcohols. Rhodium complexes are also useful. The amount of the catalyst added is suitably determined in accordance with a desired curing rate although it is generally in the range of 0.1 to 1000 ppm, preferably 1 to 200 ppm of platinum or rhodium based on the total of the entire components.

50 It is recommended that the silicone rubber composition further contains (d) a component in the form of a compound (I) or (II).

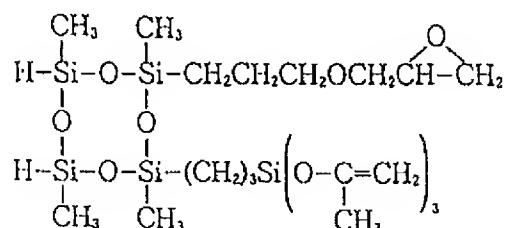
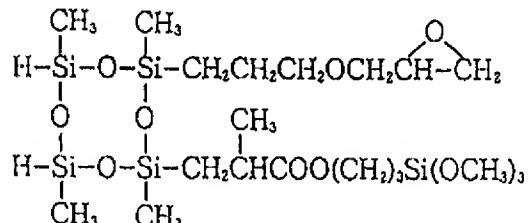
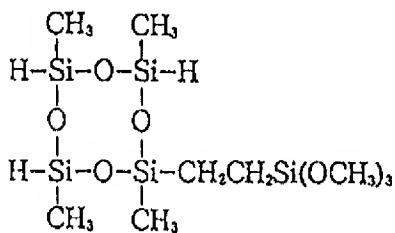
(I) is a compound containing in a molecule at least one hydrogen atom directly attached to a silicon atom and at least one of alkoxy silyl group, glycidyl group and acid anhydride group.

(II) is a compound containing in a molecule at least one hydrogen atom directly attached to a silicon atom and a divalent linkage -(CR¹R²)_n- wherein each of R¹ and R² is a hydrogen atom or a substituted or unsubstituted monovalent hydrocarbon group having 1 to 10 carbon atoms and n is an integer of from 2 to 30.

The minimum requirement for component (d) is that it improves affinity to an organic resin (polypropylene resin having an aliphatic unsaturated bond) to which the silicone rubber is to be joined. From the standpoint of joining silicone rubber to organic resin, it is preferred that the compound contains at least one hydrogen atom and preferably more than one hydrogen atom directly attached to a silicon atom in a molecule.

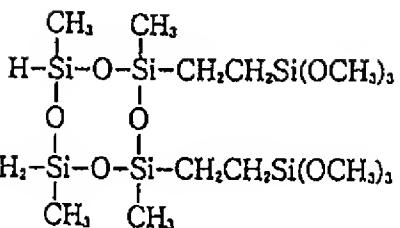
To this end, many conventional tackifier components proposed in the prior art are satisfactory. The use of these tackifier components can not provide silicone rubber with sufficient adherence to conventional polypropylene resins, but only to the specific polypropylene resin having an unsaturated group capable of hydrosilylation as contemplated herein. That is, although none of the prior art techniques can firmly join silicone rubber to polypropylene resins at a practical bond strength, the present invention selects a modified polypropylene resin so that silicone rubber, coupled with a tackifier component, can form a practically acceptable bond to the polypropylene resin.

Examples of compound (I) are given below.

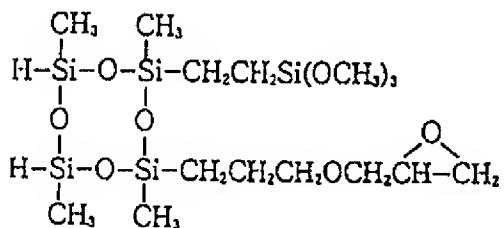


50

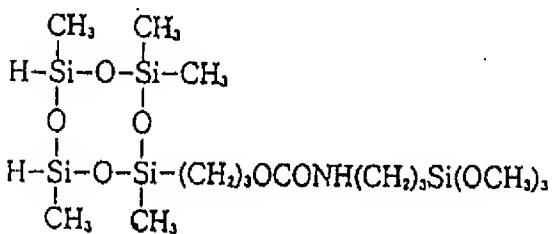
55



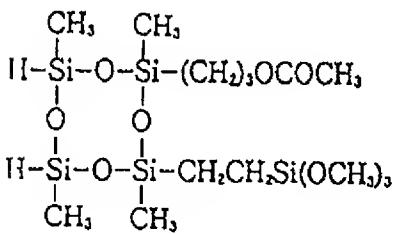
10



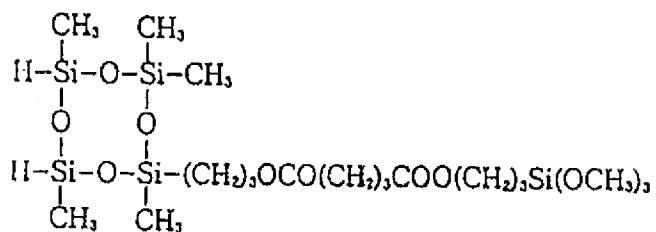
20



30



40



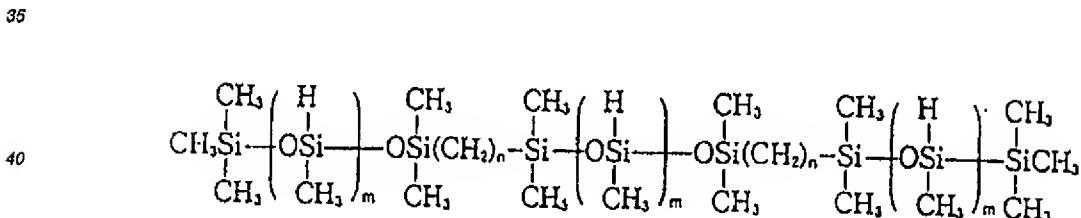
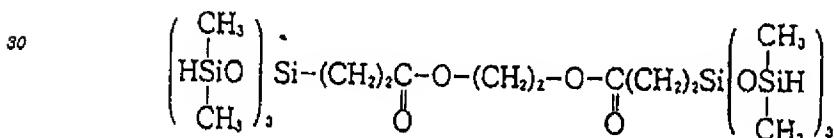
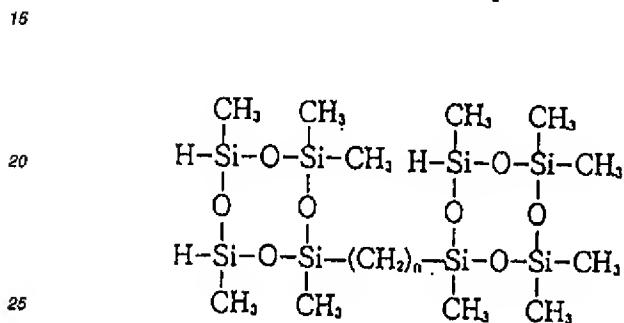
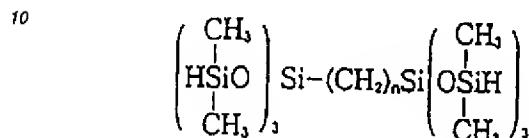
50

55 Any of the foregoing compounds may be used as tackifier component (d) to improve bonding force between silicone rubber and polypropylene resin. The use of these compounds, however, has the problem that when it is desired to mould silicone rubber to a certain shape using a metallic moulding jig, typically a metallic mould, the silicone rubber will stick to the jig. One solution to this problem is to use a moulding jig having a surface made of a less adhesive material,

for example, by applying a Teflon® resin coating to the jig surface. This solution is effective in some applications, but less reliable from the aspect of service life in other cases and unacceptable where the dimensional precision of a moulded article at its surface is of importance.

Useful in such cases is a second class of compounds free of a tackifying functional group such as trialkoxysilyl, glycidyl and acid anhydride groups. It is to be noted that the first class of compounds (I) having a tackifying functional group as mentioned above can be used without the problem insofar as the functional group is fully suppressed in reactivity by the steric restraint or electronic action of a substituent group or neighbor group.

The second class consists of compounds (II), examples of which are given below.



45 The amount of component (d) blended is properly determined without undue experimentation although it is preferably about 0.05 to 10 parts by weight per 100 parts by weight of component (a).

In one preferred embodiment where the silicone rubber should have physical strength, the silicone rubber composition further includes component (e) in the form of finely divided silica in an amount of 0 to 100 parts, preferably 5 to 50 parts, more preferably 10 to 40 parts by weight per 100 parts by weight of the total of components (a) and (b). Preferably the silica has a specific surface area of at least 50 m²/g. Exemplary of hydrophilic silica are Aerosil® 130, 200 and 300 (commercially available from Nippon Aerosil K.K. and Degussa), Cabosil® MS-5 and MS-7 (Cabot Corp.), Rheorosil®, QS-102 and 103 (Tokuyama Soda K.K.), and Nipsil® LP (Nippon Silica K.K.). Exemplary of hydrophobic silica are Aerosil® R-812, R-812S, R-972 and R-974 (Degussa), Rheorosil® MT-10 (Tokuyama Soda K.K.), and Nipsil® SS series (Nippon Silica K.K.).

55 In some cases, the curing time of the silicone rubber composition must be controlled in order that it be effective in practice. Then a suitable control agent is used. Examples of the curing control agent include vinyl-containing organopolysiloxanes such as vinylcyclotetrasiloxane, triallylisocyanurate, alkyl maleates, acetylene alcohols and silane or siloxane modified derivatives thereof, hydroperoxides, tetramethylethylenediamine, benzotriazole and mixtures thereof.

Moreover, suitable additives may be blended in the silicone rubber composition. Such additives include non-reinforcing fillers such as ground quartz, diatomaceous earth, and calcium carbonate, coloring agents including inorganic pigments such as Cobalt Blue and organic dyes, and agents for improving heat resistance and flame retardance such as cerium oxide, zinc carbonate, manganese carbonate, iron oxide, titanium oxide, and carbon black.

5 The silicone rubber composition in uncured state is integrally moulded over the polypropylene resin by any desired technique, for example, by placing the uncured silicone rubber composition in a desired form on a preform of the polypropylene resin and heating the assembly at a temperature below the softening temperature of the polypropylene resin. Placement of the uncured silicone rubber composition in a desired form can be done by moulding, coating or dipping. Another technique is by placing the uncured silicone rubber composition on a preform of the polypropylene resin and 10 heating and compressing the assembly at a temperature below the softening temperature of the polypropylene resin. Alternatively, using an injection moulding machine, the polypropylene resin is first injection moulded in a mould and the silicone rubber composition is then heated and injected into the same mould.

In moulding the unsaturated group-bearing polypropylene resin into a preform, any moulding technique commonly used for conventional thermoplastic resins may be employed. One exemplary known convenient technique includes 15 pelletizing the polypropylene resin, introducing the pellets into a mould heated above the softening point of the polypropylene resin, and cooling the mould to below the softening point of the polypropylene resin. This technique generally uses a machine known as an injection moulding machine or transfer moulding machine. Thereafter, the silicone rubber composition is moulded over the polypropylene resin preform. At this point, the silicone rubber composition may be liquid, putty or paste in uncured state. Desired for ease of moulding is a liquid or paste composition known as a liquid silicone rubber composition to those skilled in the art.

20 There has been described a polypropylene resin/silicone rubber integrally moulded article in which a polypropylene resin having an aliphatic unsaturated group or a composition containing the same is used, and an addition type silicone rubber is overlaid, joined and integrated to the polypropylene resin so that a strong bond is established between the polypropylene resin and the silicone rubber. This moulded article finds application as parts in electric, electronic, automotive and precision equipment fields since it takes advantages of the properties of both polypropylene resin and silicone rubber.

25 Such a polypropylene resin/silicone rubber integrally moulded article can be prepared in a simple reproducible manner. Moulding of the polypropylene resin or its composition and placement of the silicone rubber in contact with the polypropylene resin preform can be accomplished by injection moulding. Particularly when a compound (II) is used as tackifier component (d) in the silicone rubber composition, the silicone rubber as moulded and cured can be smoothly removed from the mould without sticking. Easy release of the silicone rubber from the metallic mould is one of the benefits.

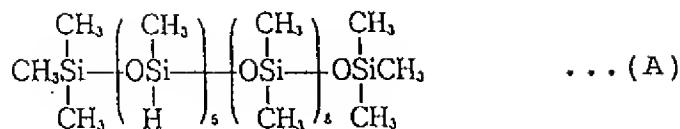
EXAMPLE

35 Examples of the present invention are given below by way of illustration. All parts are by weight.

Example 1

Preparation of silicone rubber composition

A kneader was charged with 100 parts of a dimethylsiloxane polymer blocked with a dimethylvinylsilyl group at either end and having a viscosity of 10,000 centipoise at 25°C, 40 parts of fumed silica having a specific surface area of 300 cm²/g, 8 parts of hexamethyldisilazane, and 1 part of water. The contents were agitated and mixed at room temperature for one hour, heated to 150°C, and mixed for a further 2 hours at the temperature. Thereafter, the mixture was cooled down to room temperature. To the mixture were added 20 parts of the blocked dimethylsiloxane polymer, 3 parts of a methylhydrogenpolysiloxane represented by formula (A) below and having a viscosity of about 10 centipoise at 25°C, 4 parts of a vinylmethylpolysiloxane containing 5 mol% of a vinyl group directly attached to a silicon atom and having a viscosity of 1,000 centipoise at 25°C, 0.1 part of acetylene alcohol for extending the curing time at room temperature, and 50 ppm (calculated as platinum atom) of a platinum vinylsiloxane complex. The mixture was fully mixed until uniform, obtaining a liquid addition type silicone rubber composition (I).



10 Composition (I) was pressed into a sheet at 120°C for 10 minutes. Upon measurement of mechanical properties, the sheet had a hardness of 40 on JIS A scale, an elongation of 500%, a tensile strength of 100 kgf/cm², and a tear strength of 35 kgf/cm.

15 Preparation of polypropylene resin

Random copolymerization of propylene and 1,9-decadiene was effected at 70°C in the presence of a propylene polymerizing catalyst based on a Ziegler-Natta catalyst activating titanium trichloride. The modified polypropylene resin had a 1,9-decadiene content of 2.5 mol% as measured by NMR and an MFR of 0.1 g/10 min.

20 The modified polypropylene resin was admitted into a thermoplastic resin injection moulding machine where the resin was plasticized at 200°C and injected into a plurality of sheet-shaped mould cavities whereby a plurality of sheets 25 mm wide, 100 mm long, and 2 mm thick were molded. The injection moulding conditions included an injection time of 6 seconds, a cooling time of 30 seconds, an injection pressure of 1,000 kgf/cm², a clamping pressure of 35 ton and a cavity temperature of 60°C.

25 To a jig for forming shear adhesion test pieces was fixedly attached the polypropylene resin sheet. A proper amount of the silicone composition (I) was poured into the jig where it was cured by heating for 8 minutes in a 120°C constant temperature oven, obtaining a test piece as shown in the side and plan views of FIGS. 1A and 1B. In FIG. 1, a polypropylene resin sheet 'a' is joined, to a cured part of the silicone composition 'b' (25 × 100 × 2 mm) at a bond zone 'c'. Supports 'd' and 'e' support the resin sheet 'd' and the cured silicone part 'b' respectively.

The test piece was examined by an adhesion test. The results are shown in Table 1.

30 Comparative Example 1

An adhesive test piece as shown in FIGS. 1A and 1B was prepared by the same procedure as in Example 1 except that the modified polypropylene resin was replaced by a commercially available (unmodified) polypropylene. The test pieces were examined for adhesion. The results are also shown in Table 1.

Table 1

40

	Polypropylene	Test
Example 1	modified	bonded
Comparative Example 1	unmodified	separated

45 Example 2

A two-colour injection moulding machine including a pair of injectors was used herein. Referring to FIG. 2, the injectors include nozzles 1 and 2. A mould includes left and right mould halves 3 and 4 which are formed with opposed upper and lower recesses so that they define upper and lower cavities 5 and 6 when mated along a parting line. The nozzle 1 extends through the mould along the parting line for fluid communication with the upper mould cavity 5. The nozzle 2 extends through the right mould half 4 at the centre of its right side surface for fluid communication with the lower mould cavity 6.

50 The same polypropylene resin modified with 2.5 mol% of diene as in Example 1 was admitted into the injection moulding machine where it was melted at 200°C and injected into the upper cavity 5 through the nozzle 1 to mould a polypropylene resin sheet 7 as shown in FIG. 3. The injection moulding conditions included an injection time of 6 seconds and a cooling time of 35 seconds while the upper cavity 5 and left mould half 3 were maintained at a temperature of 60°C.

55 Next, the right mould half 4 was removed to open the mould. With the resin sheet 7 left in the recess of the left

mould half 3, the mould half 3 was rotated 180° about a horizontal axis. The mould half 4 was mated again with the left mould half 3 and clamped together. Then a cavity for moulding a silicone rubber sheet was defined between the exposed surface of the resin sheet 7 and the lower recess of the right mould half 4 as shown in FIG. 4.

Then liquid addition type silicone rubber composition (I) was injected against the exposed surface of the resin sheet 7 through the nozzle 2 to mould a rubber sheet 8 as shown in FIG. 5. The moulding conditions included an injection time of 6 seconds and a curing time of 100 seconds while the left and right mould halves 3 and 4 were at temperatures of 60°C and 80°C, respectively.

The foregoing procedure yielded a composite moulded article as shown in FIG. 6 wherein the resin and rubber sheets 7 and 8 were firmly joined together. Both the sheets were of the same dimensions: 2.5 mm wide, 15 cm long, and 2 mm thick. The composite moulded article was firmly integrated and had satisfactory dimensional precision and production yields.

Comparative Example 2

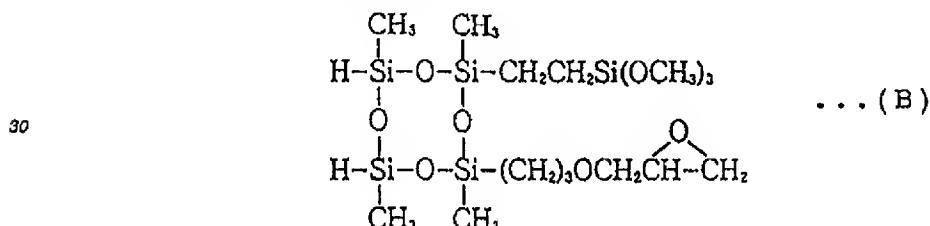
A composite moulded article as shown in FIG. 6 was prepared by the same procedure as in Example 2 except that the modified polypropylene resin was replaced by an unmodified polypropylene. The article was examined for adhesion to find that the resin sheet was readily separated from the silicone rubber sheet.

Example 3

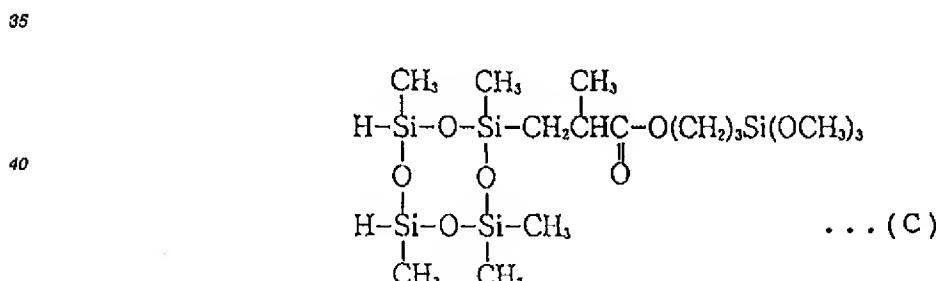
Preparation of silicone rubber composition

To 100 parts of silicone rubber composition (I) in Example 1 was added 2 parts of a compound of formula (B) or (C) shown below as tackifier component.

25



30



35

Preparation of polypropylene (PP) resin

60

Random copolymerization of propylene and 1,9-decadiene was effected at 70°C in the presence of a propylene polymerizing catalyst based on a Ziegler-Natta catalyst activating titanium trichloride. The modified polypropylene resin had a 1,9-decadiene content of 1.5 mol% as measured by NMR and an MFR of 0.3 g/10 min.

The modified polypropylene resin was admitted into a thermoplastic resin injection moulding machine where the resin was plasticized at 200°C and injected into a plurality of sheet-shaped mould cavities whereby a plurality of sheets of 25 mm wide, 100 mm long, and 2 mm thick were moulded. The injection moulding conditions included an injection time of 6 seconds, a cooling time of 30 seconds, an injection pressure of 1,000 kg/cm², a clamping pressure of 35 ton, and a cavity temperature of 60°C.

To a jig for forming shear adhesion test pieces was fixedly attached the polypropylene resin sheet or one of chromium-plated metal, nickel-plated metal and aluminium alloy sheets of the same dimensions. A proper amount of the silicone composition was poured into the jig where it was cured by heating for 8 minutes in a 120°C constant temperature oven, obtaining a test piece as shown in the side and plan views of FIGS. 1A and 1B.

5 The test pieces were examined by an adhesion test. The results are shown in Table 2.

Comparative Example 3

Adhesive test pieces as shown in FIGS. 1A and 1B were prepared by the same procedure as in Example 3 except
10 that the modified polypropylene resin was replaced by an unmodified polypropylene. The test pieces were examined for adhesion. The results are also shown in Table 2.

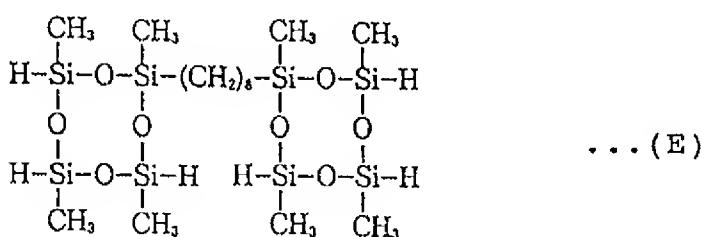
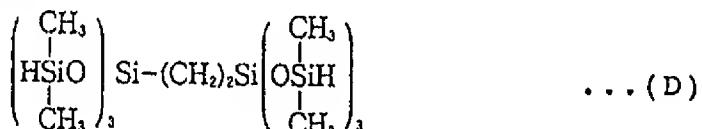
Table 2

	Sheet	Test	Remarks
15	Modified PP	bonded	Example 3
	Chromium-plated metal	bonded	Example 3
20	Nickel-plated metal	bonded	Example 3
	Aluminium alloy	bonded	Example 3
	Unmodified PP	separated	Comparative Example 3

25 Example 4

Several sheets 25 mm wide, 100 mm long, and 2 mm thick were injection moulded from the same polypropylene resin by the same method under the same conditions as in Example 3.

Separately, to 100 parts of composition (I) was added 0.5 or 1 part of a compound of formula (D) or (E) shown
30 below as tackifier component.



50 To a jig for forming shear adhesion test pieces was fixedly attached the polypropylene resin sheet or one of chromium-plated metal, nickel-plated metal and aluminium alloy sheets of the same dimensions. A proper amount of the silicone rubber composition was poured into the jig where it was cured by heating for 8 minutes in a 120°C constant temperature oven, obtaining a test piece as shown in the side and plan views of FIGS. 1A and 1B. The test pieces were
55 examined for adhesion. The results are shown in Table 3.

Comparative Example 4

5 A sheet 25 mm wide, 100 mm long, and 2 mm thick was injection moulded by the same procedure as in Example 4 except that the modified polypropylene resin (filler free) was replaced by an unmodified polypropylene (filler free). Liquid addition type silicone rubber composition (I) in Example 1 was cured to the sheet by heating for 8 minutes in a 120°C constant temperature oven, obtaining a test piece as shown in FIGS. 1A and 1B. It was examined for adhesion. The result is also shown in Table 3.

10

Table 3

15

Example 4				
Tackifier (D)	0.5 pbw	1 pbw	-	-
Tackifier (E)	-	-	0.5 pbw	1 pbw
Cr-plated metal	separated	separated	separated	separated
Ni-plated metal	separated	separated	separated	separated
Aluminum alloy	separated	separated	separated	separated
Modified PP	bonded	bonded	bonded	bonded
Comparative Example 4				
Unmodified PP	separated	separated	separated	separated

20

25

Example 5

The same polypropylene resin modified with 1.5 mol% of diene as in Example 3 was admitted into the injection moulding machine of FIG. 2 where it was melted at 200°C and injected into the upper cavity 5 through the nozzle 1 to mould a polypropylene resin sheet 7 as shown in FIG. 3. The injection moulding conditions included an injection time of 6 seconds and a cooling time of 35 seconds while the upper cavity 5 and left mould half 3 were maintained at a temperature of 60°C.

Next, the right mould half 4 was removed to open the mould. With the resin sheet 7 left in the recess of the left mould half 3, the mould half 3 was rotated 180° about a horizontal axis. The right mould half 4 was mated again with the left mould half 3 and clamped together. Then a cavity for moulding a silicone rubber sheet was defined between the exposed surface of the resin sheet 7 and the lower recess of the right mould half 4 as shown in FIG. 4.

Then a composition containing 100 parts of liquid addition type silicone rubber composition (I) and 0.5 or 1 part of tackifier (D) or (E) used in Example 4 was injected against the exposed surface of the resin sheet 7 through the nozzle 2 to mould a rubber sheet 8 as shown in FIG. 5. The moulding conditions included an injection time of 6 seconds and a curing time of 100 seconds while the left and right mould halves 3 and 4 were at temperatures of 60°C and 80°C respectively.

The foregoing procedure yielded a composite moulded article as shown in FIG. 6 wherein the resin and rubber sheets 7 and 8 were firmly joined together. Both the sheets were of the same dimensions: 2.5 mm wide, 15 cm long, and 2 mm thick. All composite moulded articles obtained from the compositions having 0.5 and 1 part of tackifiers (D) and (E) were firmly integrated and had satisfactory dimensional precision and production yields. The rubber sheets could be readily released from the mould made of chromium-plated carbon steel.

Comparative Example 5

50 A composite moulded article as shown in FIG. 6 was prepared by the same procedure as in Example 5 except that the modified polypropylene resin was replaced by an unmodified polypropylene. The article was examined for adhesion to find that the resin sheet was readily separated from the silicone rubber sheet.

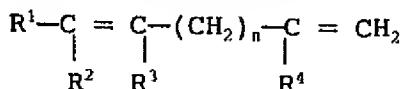
Although some preferred embodiments have been described, many modifications and variations may be made thereto in the light of the above teachings. It is therefore to be understood that within the scope of the appended claims, the invention may be practised otherwise than as specifically described.

Claims

1. A polypropylene resin/silicone rubber integrally moulded article in which

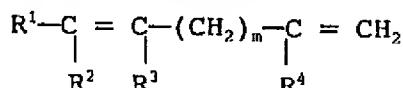
5 (a) a polypropylene component made of polypropylene resin selected from

(i) random copolymers of propylene with non-conjugated diene of the formula



10 where groups R^1 to R^4 are selected independently from H and C_{1-6} alkyl, and n is an integer in the range from 1 to 20, and

15 (ii) graft copolymers of polypropylene graft-polymerised with non-conjugated diene of the formula



20 where groups R^1 to R^4 are selected independently from H and C_{1-6} alkyl, and m is an integer in the range from 1 to 20;

25 or of a resin composition containing such a polypropylene resin, is integrally joined to
 (b) an addition-type silicone rubber obtainable from a composition comprising

30 (i) alkenyl group-containing organopolysiloxane;

35 (ii) organohydrogenpolysiloxane having per molecule at least two hydrogen atoms directly attached to silicon atom, and

(iii) addition reaction catalyst.

2. An article according to claim 1 in which the polypropylene component comprises said random copolymer of propylene with non-conjugated diene, residues of the non-conjugated diene constituting from 0.01 to 20 mol% of the random copolymer.

3. An article according to claim 1 in which the polypropylene component comprises said graft copolymer, residues of the non-conjugated diene constituting from 0.01 to 20 mol% of the graft copolymer.

4. An article according to any one of claims 1 to 3 in which the composition for the silicone rubber comprises a compound containing per molecule at least one Si-H group and at least one alkoxysilyl, glycidyl or acid anhydride group.

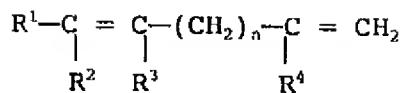
5. An article according to any one of claims 1 to 3 in which the composition for the silicone rubber comprises a compound containing per molecule at least one Si-H group and a divalent linkage $-(CR^1R^2)_n-$, where R^1 and R^2 are selected from H and substituted and unsubstituted C_{1-10} monovalent hydrocarbon groups and n is an integer in the range from 2 to 30.

6. An article according to any one of the preceding claims in which the silicone rubber comprises from 5 to 50 parts by weight of finely-divided silica per 100 parts by weight of the combined organopolysiloxane and organohydrogenpolysiloxane components (b)(i),(ii).

7. A method of making a polypropylene resin/silicone rubber integrally moulded article, comprising the steps of

55 (a) moulding a polypropylene component preform from a polypropylene resin selected from

(i) random copolymers of propylene with non-conjugated diene of the formula

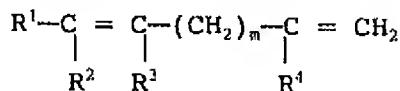


5

where groups R^1 to R^4 are selected independently from H and C_{1-6} alkyl, and n is an integer in the range from 1 to 20, and

(ii) graft copolymers of polypropylene graft-polymerised with non-conjugated diene of the formula

10



15

where groups R^1 to R^4 are selected independently from H and C_{1-6} alkyl, and m is an integer in the range from 1 to 20;

20

or from a resin composition containing such a polypropylene resin;

(b) contacting an adhesive addition-curable silicone rubber composition, comprising

25

(i) alkenyl group-containing organopolysiloxane

(ii) organohydrogenpolysiloxane having per molecule at least two hydrogen atoms directly attached to silicon atom, and

(iii) addition reaction catalyst with a surface of the preform, and

30

(c) curing the silicone rubber composition at a temperature lower than the softening point of the polypropylene component.

8. A method according to claim 7 in which the polypropylene component comprises said random copolymer of propylene with non-conjugated diene, residues of the non-conjugated diene constituting from 0.01 to 20 mol% of the random copolymer.

35

9. A method according to claim 7 in which the polypropylene component comprises said graft copolymer, residues of the non-conjugated diene constituting from 0.01 to 20 mol% of the graft copolymer.

10. A method according to any one of claims 7 to 9 in which the silicone rubber composition comprises a compound (I) containing per molecule at least one Si-H group and at least one alkoxyisilyl, glycidyl or acid anhydride group.

40

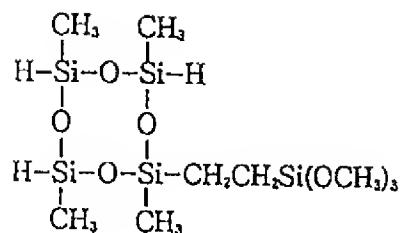
11. A method according to claim 10 in which the compound (I) is selected from

45

50

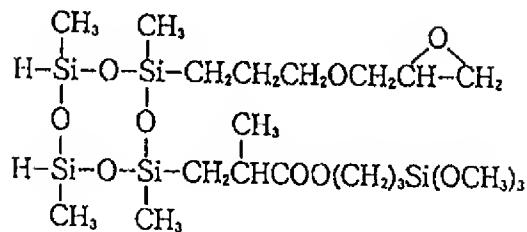
55

5



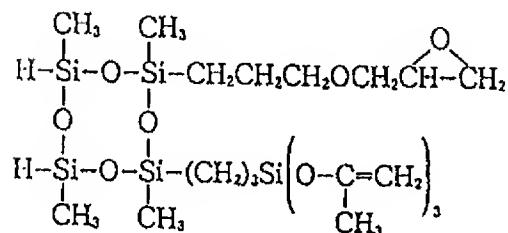
10

15



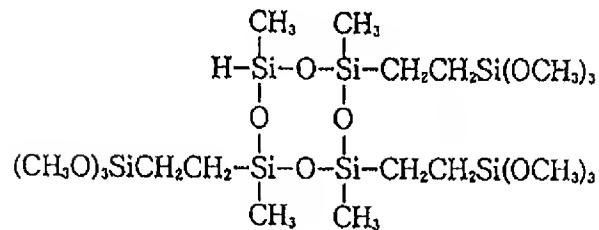
20

25



30

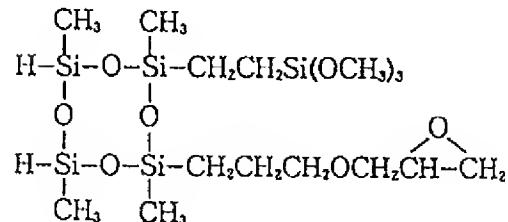
35



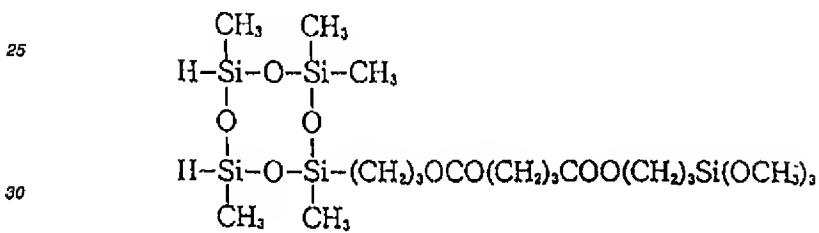
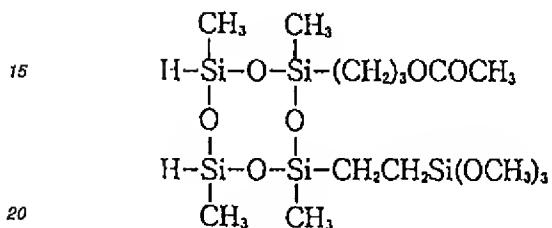
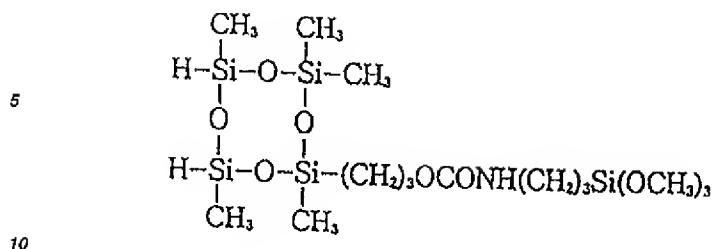
40

45

50



55



35

12. A method according to any one of claims 7 to 9 in which the silicone rubber composition comprises a compound (II) containing per molecule at least one Si-H group and a divalent linkage $-(\text{CR}^1\text{R}^2)_n-$, where R¹ and R² are selected from H and substituted and unsubstituted C₁₋₁₀ monovalent hydrocarbon groups and n is an integer in the range from 2 to 30.

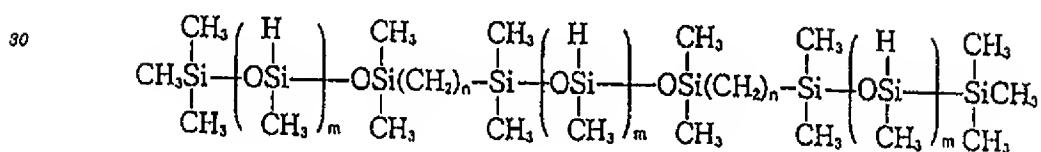
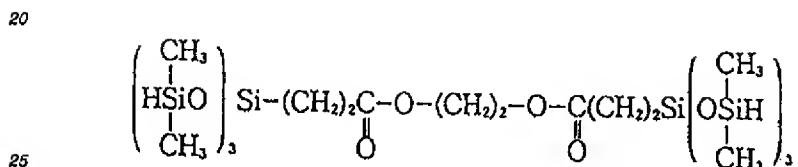
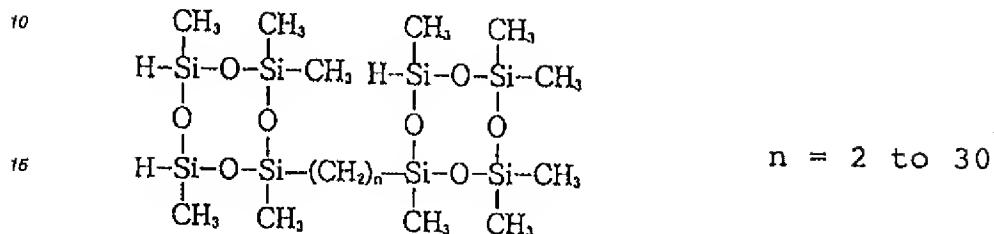
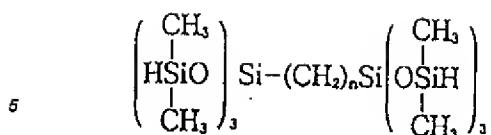
40

13. A method according to claim 12 in which the compound (II) is selected from

45

50

55



40 14. A method according to claim 12 or claim 13 in which the amount of compound (I) or (II) in the silicone rubber composition is in the range from 0.05 to 10 parts by weight per 100 parts by weight of the organopolysiloxane (b)(i).

15. A method according to any one of claims 7 to 14 in which in the silicone rubber composition:

45 the organopolysiloxane (i) accords with the compositional formula



where R are substituted or unsubstituted hydrocarbon groups, from 0.1 to 1 mol% of which are alkenyl, and $1.9 \leq a \leq 2.4$, and

50 the organohydrogenpolysiloxane (ii) is present in an amount constituting from 0.8 to 2 equivalents per equivalent of alkenyl group in the organopolysiloxane (i).

16. A method according to any one of claims 7 to 15 in which the steps of moulding the preform and contacting the silicone rubber composition with it are done by injection moulding.

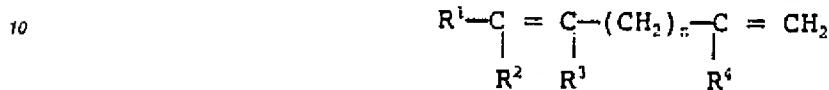
55 17. A method according to any one of claims 7 to 16 in which the non-conjugated diene is 1,9-decadiene or 1,13-tetradecadiene.

Patentansprüche

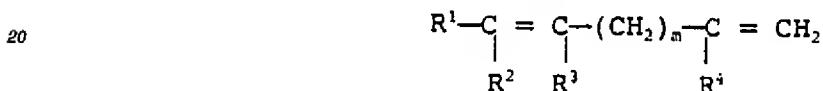
1. Einstückiger Formteil aus Polypropylenharz/Silikongummi, worin

5 (a) eine Polypropylenkomponente, die aus Polypropylenharz besteht, das ausgewählt ist aus:

(i) statistischen Copolymeren von Propylen mit nichtkonjugiertem Dien der Formel



15 worin die Gruppen R¹ bis R⁴ unabhängig voneinander aus H und C₁₋₆-Alkyl ausgewählt sind und n eine ganze Zahl im Bereich von 1 bis 20 ist, und
 (ii) Ppropf-Copolymeren von Polypropylen, das mit nichtkonjugiertem Dien der Formel



25 ppropfpolymerisiert ist, worin die Gruppen R¹ bis R⁴ unabhängig voneinander aus H und C₁₋₆-Alkyl ausgewählt sind und m eine ganze Zahl im Bereich von 1 bis 20 ist;
 oder aus einer Harzzusammensetzung, die ein solches Polypropylenharz enthält, einstückig verbunden ist mit

30 (b) einem Silikongummi vom Additionstyp, der aus einer Zusammensetzung erhältlich ist, die umfaßt:

(i) alkenylgruppenhaltiges Organopolysiloxan;
 (ii) Organohydrogenpolysiloxane, die pro Molekül zumindest zwei direkt an Siliziumatom gebundene Wasserstoffatome aufweisen, und
 (iii) Additionskatalysator.

35 2. Formteil nach Anspruch 1, in dem die Polypropylenkomponente das statistische Copolymer von Propylen mit nichtkonjugiertem Dien umfaßt, wobei Reste des nichtkonjugierten Dien 0,01 bis 20 Mol-% des statistischen Copolymer ausmachen.

40 3. Formteil nach Anspruch 1, worin die Polypropylenkomponente das Ppropf-Copolymer umfaßt, wobei Reste des nichtkonjugierten Dien 0,01 bis 20 Mol-% des Ppropf-Copolymers ausmachen.

45 4. Formteil nach einem der Ansprüche 1 bis 3, bei dem die Zusammensetzung für den Silikongummi eine Verbindung umfaßt, die pro Molekül zumindest eine Si-H-Gruppe und zumindest eine Alkoxy-silyl-, Glycidyl- oder Säureanhydridgruppe enthält.

50 5. Formteil nach einem der Ansprüche 1 bis 3, bei dem die Zusammensetzung für den Silikongummi eine Verbindung umfaßt, die pro Molekül zumindest eine Si-H-Gruppe und einen zweiwertigen Linker -(CR¹R²)_n- enthält, worin R¹ und R² aus H und substituierten und unsubstituierten einwertigen C₁₋₁₀-Kohlenwasserstoffgruppen ausgewählt sind und n eine ganze Zahl im Bereich von 2 bis 30 ist.

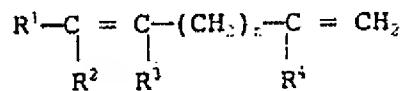
55 6. Formteil nach einem der vorangegangenen Ansprüche, bei dem der Silikongummi 5 bis 50 Gewichtsteile feinteilige Kieselsäure pro 100 Gewichtsteile der Kombination aus Organopolysiloxan- und Organohydrogenpolysiloxan-Komponente (b)(i), (ii) umfaßt.

7. Verfahren zur Herstellung eines einstückig geformten Polypropylenharz/Silikongummi-Formteils, folgende Schritte umfassend:

(a) das Formen eines Polypropylenkomponenten-Vorformlings aus einem Polypropylenharz, ausgewählt aus:

(I) statistischen Copolymeren von Propylen mit nichtkonjugiertem Dien der Formel

5

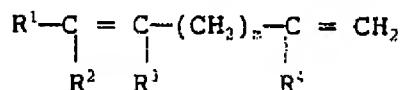


10

worin die Gruppen R¹ bis R⁴ unabhängig voneinander aus H und C₁₋₆-Alkyl ausgewählt sind und n eine ganze Zahl im Bereich von 1 bis 20 ist, und

(ii) Ppropf-Copolymeren von Polypropylen, das mit nichtkonjugiertem Dien der Formel

15



20

ppropfpolymerisiert ist, worin die Gruppen R¹ bis R⁴ unabhängig voneinander aus H und C₁₋₆-Alkyl ausgewählt sind und meine ganze Zahl im Bereich von 1 bis 20 ist; oder aus einer Harzzusammensetzung, die ein solches Polypropylenharz enthält;

25

(b) das In-Kontakt-Bringen einer haftfähigen additionshärtbaren Silikonkautschuk-Zusammensetzung, umfassend

30

(i) alkenylgruppenhaltiges Organopolysiloxan,
(ii) Organohydrogenpolysiloxane, die pro Molekül zumindest zwei direkt an Siliziumatom gebundene Wasserstoffatome aufweisen, und
(iii) einen Additionskatalysator,
mit einer Oberfläche des Vorformlings, und

35

(c) das Härtten der Silikonkautschukzusammensetzung bei einer Temperatur unter dem Erweichungspunkt der Polypropylenkomponente.

40

8. Verfahren nach Anspruch 7, bei dem die Polypropylenkomponente das statistische Copolymer von Propylen mit nichtkonjugiertem Dien umfaßt, wobei Reste des nichtkonjugierten Diens 0,01 bis 20 Mol-% des statistischen Copolymers ausmachen.
9. Verfahren nach Anspruch 7, bei dem die Polypropylenkomponente das Ppropf-Copolymer umfaßt, wobei Reste des nichtkonjugierten Diens 0,01 bis 20 Mol-% des Ppropf-Copolymers ausmachen.

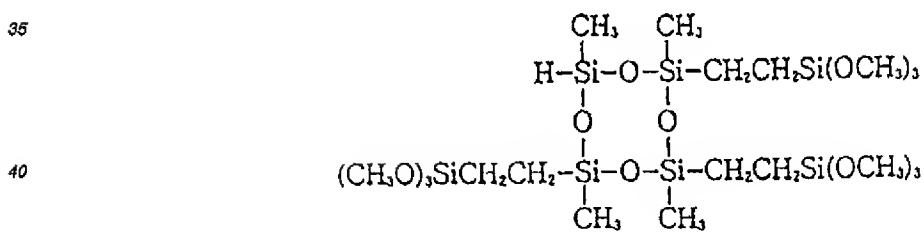
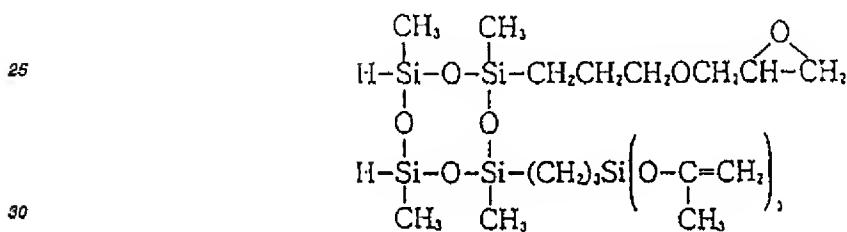
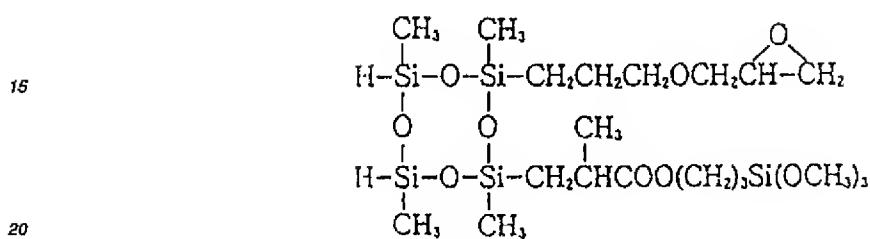
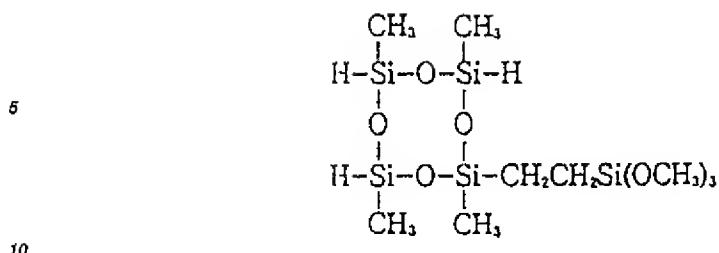
45

10. Verfahren nach einem der Ansprüche 7 bis 9, bei dem die Silikonkautschukzusammensetzung eine Verbindung (I) umfaßt, die pro Molekül zumindest eine Si-H-Gruppe und zumindest eine Alkoxyisilyl-, Glycidyl- oder Säureanhydridgruppe enthält.

11. Verfahren nach Anspruch 10, bei dem die Verbindung (I) ausgewählt ist aus:

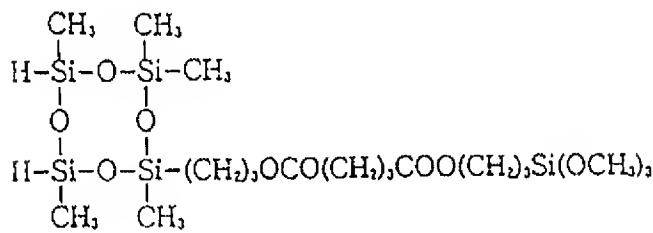
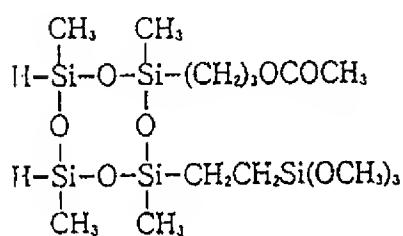
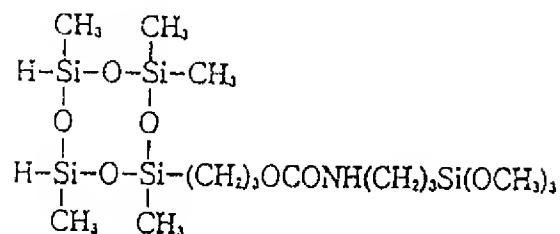
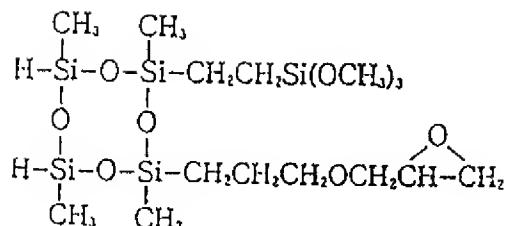
50

55



50

55

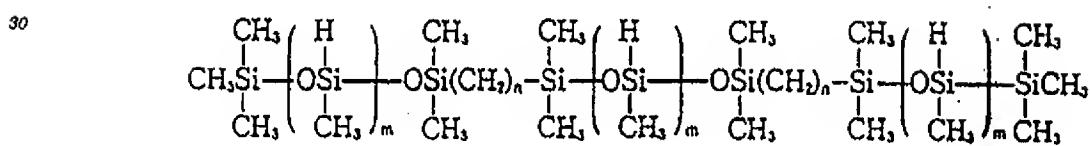
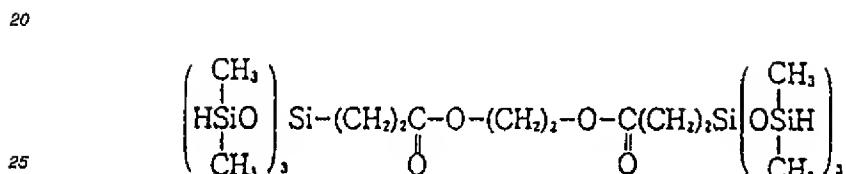
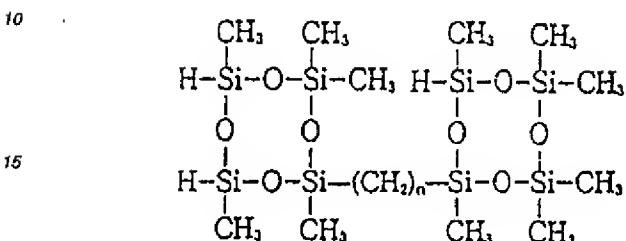
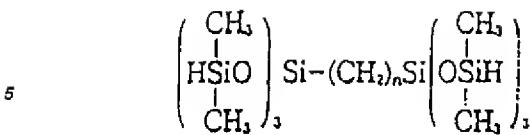


45

12. Verfahren nach einem der Ansprüche 7 bis 9, bei dem, die Silikonkautschukzusammensetzung eine Verbindung (II) umfaßt, die pro Molekül zumindest eine Si-H-Gruppe und einen zweiwertigen Linker -(CR¹R²)_n- enthält, worin R¹ und R² aus H und substituierten oder unsubstituierten einwertigen C₁₋₁₀-Kohlenwasserstoffgruppen ausgewählt sind und n eine ganze Zahl im Bereich von 2 bis 30 ist.

50

13. Verfahren nach Anspruch 12, bei dem die Verbindung (II) ausgewählt ist aus



40

14. Verfahren nach Anspruch 12 oder 13, bei dem die Menge an Verbindung (I) oder (II) in der Silikonkautschukzusammensetzung im Bereich von 0,05 bis 10 Gewichtsteilen pro 100 Gewichtsteile des Organosiloxans (b)(i) liegt.

15. Verfahren nach einem der Ansprüche 7 bis 14, bei dem in der Silikonkautschukzusammensetzung:
das Organopolysiloxan (i) der Zusammensetzungsumformel



entspricht, worin R substituierte oder unsubstituierte Kohlenwasserstoffgruppen sind, von denen 0,1 bis 1 Mol-% Alkenyl sind, und gilt: $1,9 \leq a \leq 2,4$, und das Organohydrogenpolysiloxan (ii) in einer Menge von 0,8 bis 2 Äquivalenten pro Äquivalent Alkenylgruppen im Organopolysiloxan (i) vorhanden ist.

50

16. Verfahren nach einem der Ansprüche 7 bis 15, bei dem die Schritte des Formens des Vorformlings und des Damit-In-Kontakt-Bringen der Silikonkautschukzusammensetzung durch Spritzguß erfolgen.

17. Verfahren nach einem der Ansprüche 7 bis 16, bei dem das nichtkonjugierte Den 1,9-Decadien oder 1,13-Tetrade-

55

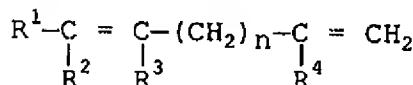
cadien ist.

Revendications

1. Un article moulé intégralement en résine de polypropylène/caoutchouc de silicone dans lequel

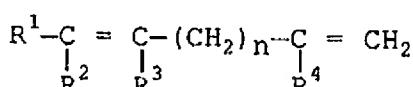
5 (a) un composant de polypropylène formé d'une résine de polypropylène sélectionnée parmi

(i) des copolymères statistiques de propylène avec un diène non conjugué de la formule



15 où les groupes R¹ à R⁴ sont indépendamment sélectionnés parmi H et alkyle C₁₋₆, et n est un entier de l'ordre de 1 à 20, et

(ii) des copolymères greffés de polypropylène polymérisé par greffe avec un diène non conjugué de la formule



25 où les groupes R¹ à R⁴ sont sélectionnés indépendamment parmi H et alkyle C₁₋₆, et m est un entier de l'ordre de 1 à 20;

ou d'une composition de résine contenant une telle résine de polypropylène, est intégralement joint à

(b) un caoutchouc de silicone du type par additon pouvant être obtenu d'une composition comprenant

30 (i) un organopolysiloxane contenant un groupe alcényle;

(ii) un organohydrogénopolysiloxane ayant par molécule au moins deux atomes d'hydrogène directement attachés à l'atome de silicium, et

35 (iii) un catalyseur de réaction par addition.

2. Un article selon la revendication 1, dans lequel le composant de polypropylène comprend ledit copolymère statistique de propylène avec le diène non conjugué, les résidus du diène non conjugué constituant 0,01 à 20% en moles du copolymère statistique.

3. Un article selon la revendication 1 dans lequel le composant de polypropylène comprend ledit copolymère greffé, les résidus du diène non conjugué constituant de 0,01 à 20% en mole du copolymère greffé.

4. Un article selon l'une quelconque des revendications 1 à 3, dans lequel la composition pour le caoutchouc de silicone comprend un composé contenant, par molécule, au moins un groupe Si-H et au moins un groupe alcoxysilyle, glycidyle ou anhydride d'acide.

5. Un article selon l'une quelconque des revendications 1 à 3, dans lequel la composition pour le caoutchouc de silicone comprend un composé contenant, par molécule, au moins un groupe Si-H et un enchaînement divalent -(CR¹R²)_n, où R¹ et R² sont sélectionnés parmi H et de groupes hydrocarbures monovalents C₁₋₁₀ substitués et non substitués et n est un entier de l'ordre de 2 à 30.

6. Un article selon l'une quelconque des revendications précédentes, dans lequel le caoutchouc de silicone comprend 5 à 50 parties en poids de silice finement divisée pour 100 parties en poids des composants combinés d'organopolysiloxane et d'organohydrogénopolysiloxane (b) (i), (ii).

7. Méthode de fabrication d'un article intégralement moulé en résine de polypropylène/caoutchouc de silicone com-

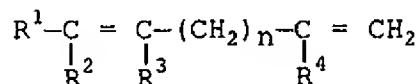
prenant les étapes de :

(a) mouler la préforme d'un composant de polypropylène à partir d'une résine de polypropylène sélectionnée parmi

5

(i) des copolymères statistiques de propylène avec un diène non conjugué de la formule

10

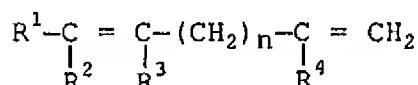


où les groupes R¹ et R⁴ sont indépendamment sélectionnés parmi H et alkyle C₁₋₆, et n est un entier de l'ordre de 1 à 20, et

15

(ii) des copolymères greffés de polypropylène polymérisés par greffe avec un diène non conjugué de la formule

20



25

où les groupes R¹ et R⁴ sont sélectionnés indépendamment parmi H et alkyle C₁₋₆, et m est un entier de l'ordre de 1 à 20;

ou d'une composition de résine contenant une telle résine de polypropylène;

(b) mettre en contact une composition adhésive d'un caoutchouc de silicone durcissable par addition, comprenant

30

(i) un organopolysiloxane contenant un groupe alcényle;

35

(ii) un organohydrogénopolysiloxane ayant par molécule au moins deux atomes d'hydrogène directement attachés à l'atome de silicium, et

(iii) un catalyseur de réaction par addition avec une surface de la préforme, et

(c) durcir la composition du caoutchouc de silicone à une température plus basse que le point d'amollissement du composant de polypropylène.

40

8. Méthode selon la revendication 7, dans laquelle le composant de polypropylène comprend ledit copolymère statistique de propylène avec un diène non conjugué, les résidus du diène non conjugué constituant 0,01 à 20% en modes du copolymère statistique.

45

9. Méthode selon la revendication 7, dans laquelle le composant de polypropylène comprend ledit copolymère greffé, les résidus du diène non conjugué constituant de 0,01 à 20% en modes du copolymère greffé.

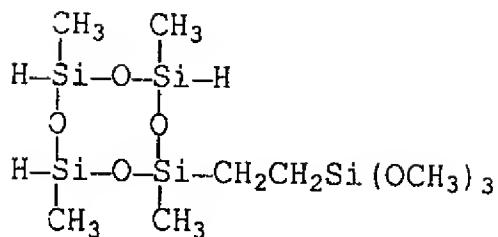
50

10. Méthode selon l'une quelconque des revendications 7 à 9, dans laquelle la composition de caoutchouc de silicone comprend un composé (I) contenant, par molécule au moins un groupe Si-H, et au moins un groupe alcoxysilyle, glycidyle ou anhydride d'acide.

11. Méthode selon la revendication 10, dans laquelle le composé (I) est sélectionné parmi

55

5



10

15

20

25

30

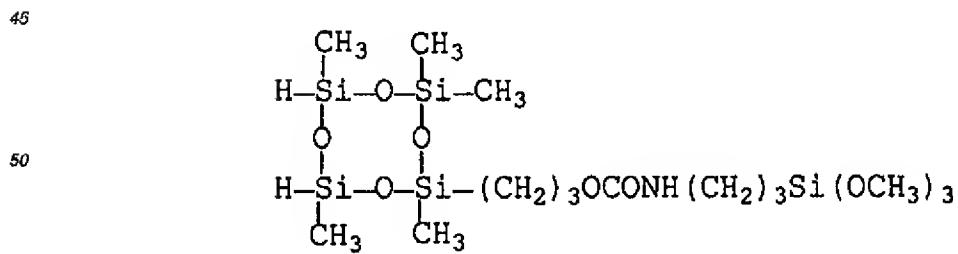
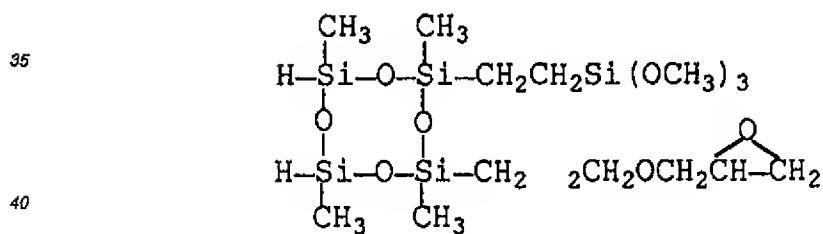
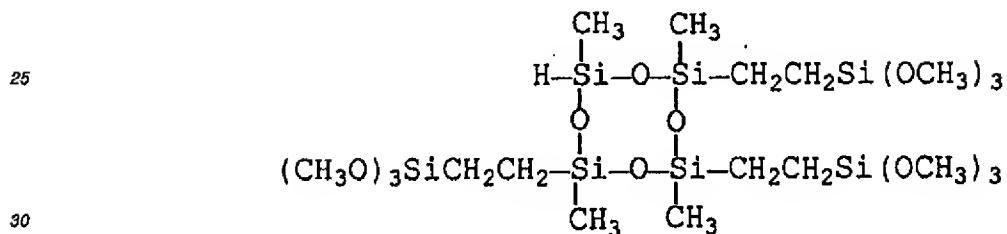
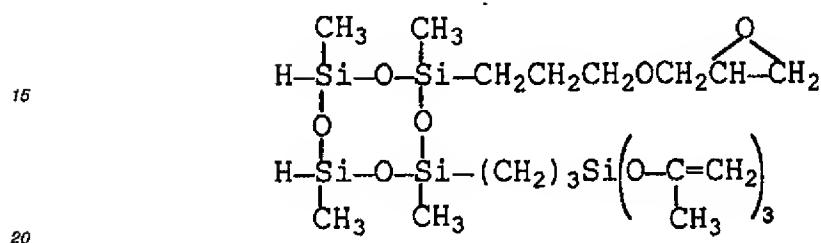
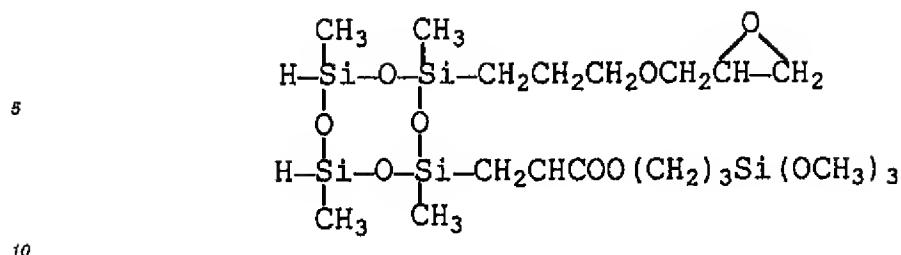
35

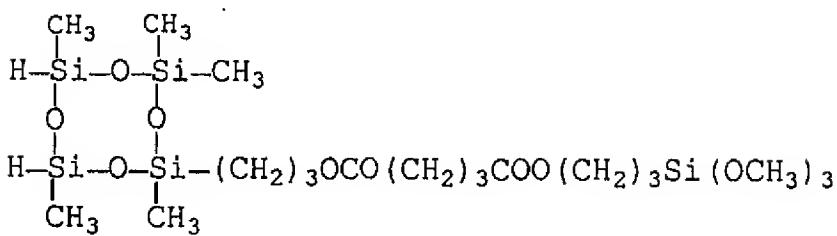
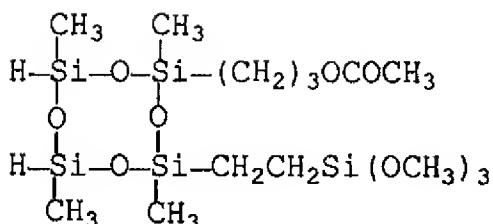
40

45

50

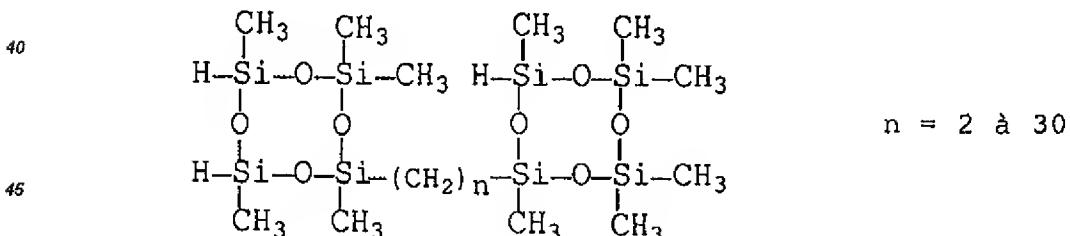
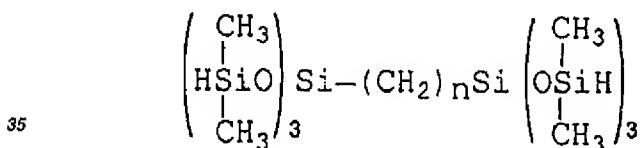
55





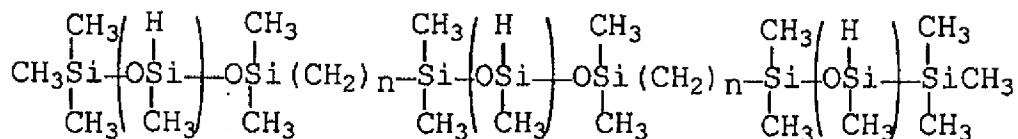
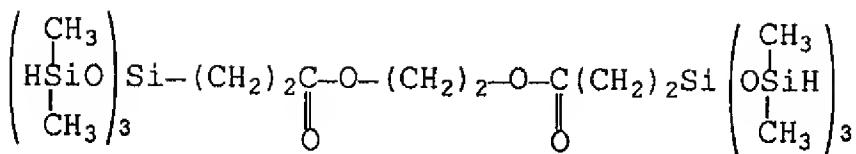
25 12. Méthode selon l'une quelconque des revendications 7 à 9, dans laquelle la composition du caoutchouc de silicium comprend un composé (II) contenant par molécule au moins un groupe Si-H et un enchaînement divalent -
 $(\text{CR}^1\text{R}^2)_n$, où R¹ et R² sont sélectionnés parmi H et des groupes hydrocarbures monovalents C₁₋₁₀ substitués et non substitués et n est un entier de l'ordre de 2 à 30.

30 13. Méthode selon la revendication 12, dans laquelle le composé (II) est sélectionné parmi



50

55



15

20 14. Méthode selon la revendication 12 ou la revendication 13, dans laquelle la quantité du composé (I) ou (II) dans la composition du caoutchouc de silicone est comprise entre 0,05 et 10 parties en poids pour 100 parties en poids de l'organopolysiloxane (b)(i).

25 15. Méthode selon l'une quelconque des revendications 7 à 14, dans laquelle, dans la composition du caoutchouc de silicone :

l'organopolysiloxane (i) est en accord avec la formule de composition



30 où R sont des groupes hydrocarbures substitués ou non substitués, dont 0,1 à 1 mole % sont alcényle, et 1,9 ≤ a ≤ 2,4, et
l'organohydrogénopolysiloxane (ii) est présent en une quantité constituant 0,8 à 2 équivalents par équivalent du groupe alcényle dans l'organopolysiloxane (i).

35 16. Méthode selon l'une quelconque des revendications 7 à 15, dans laquelle les étapes de mouler la préforme et de mettre la composition de caoutchouc de silicone en contact avec elle sont faites par moulage par injection.

40 17. Méthode selon l'une quelconque des revendications 7 à 16, dans laquelle le diène non conjugué est le 1,9-déca-diène ou le 1,13-tétradécadiène.

45

50

55

FIG.1 (A)

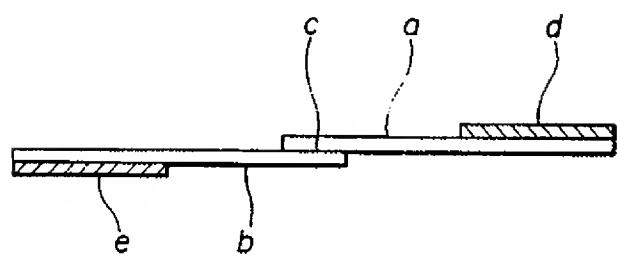


FIG.1 (B)

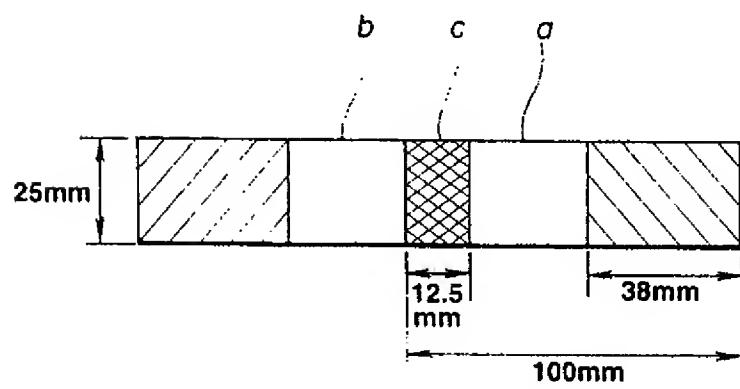


FIG.2

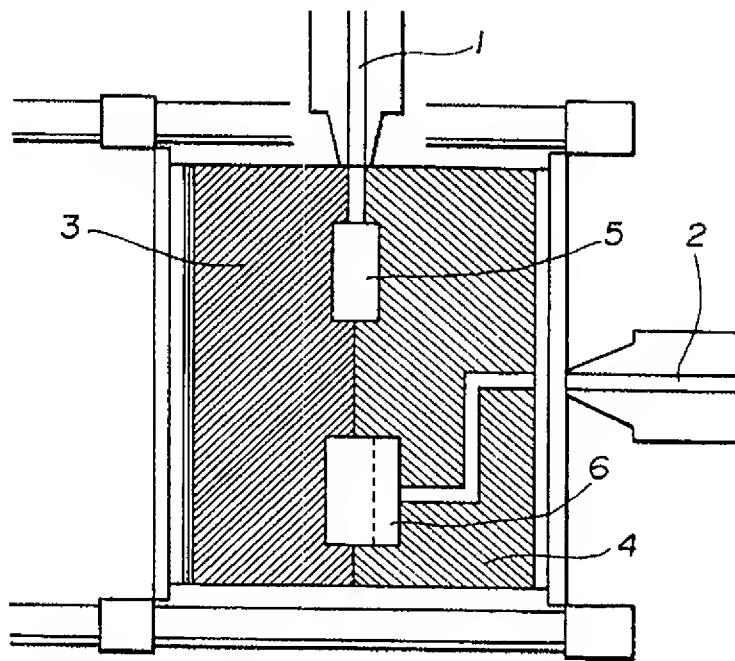


FIG.3

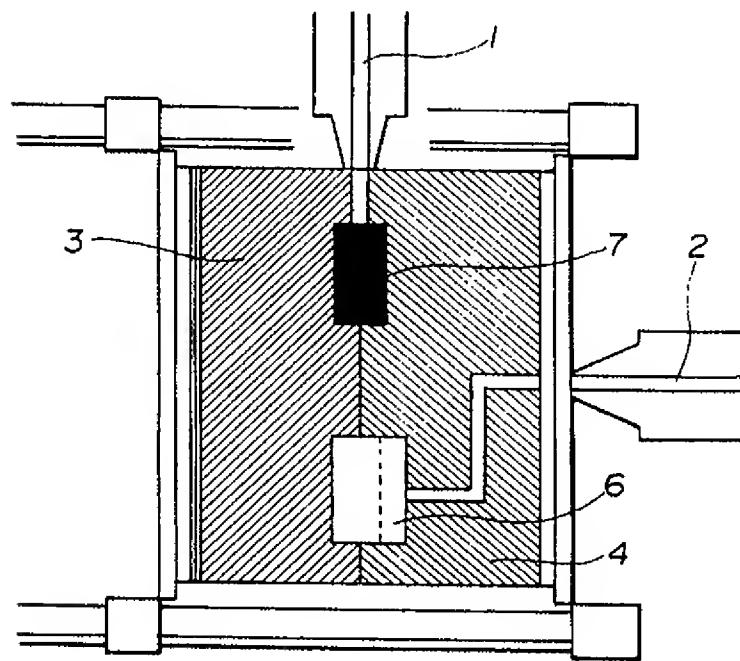


FIG.4

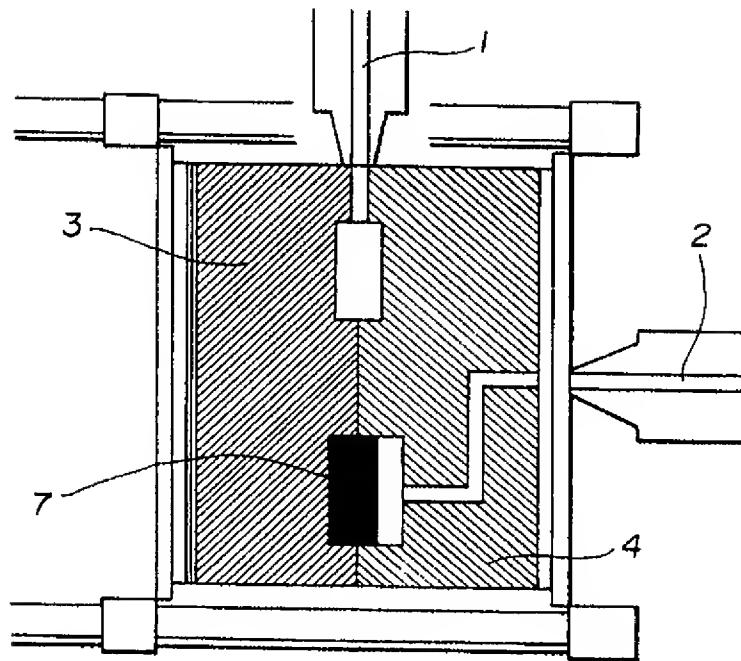


FIG.5

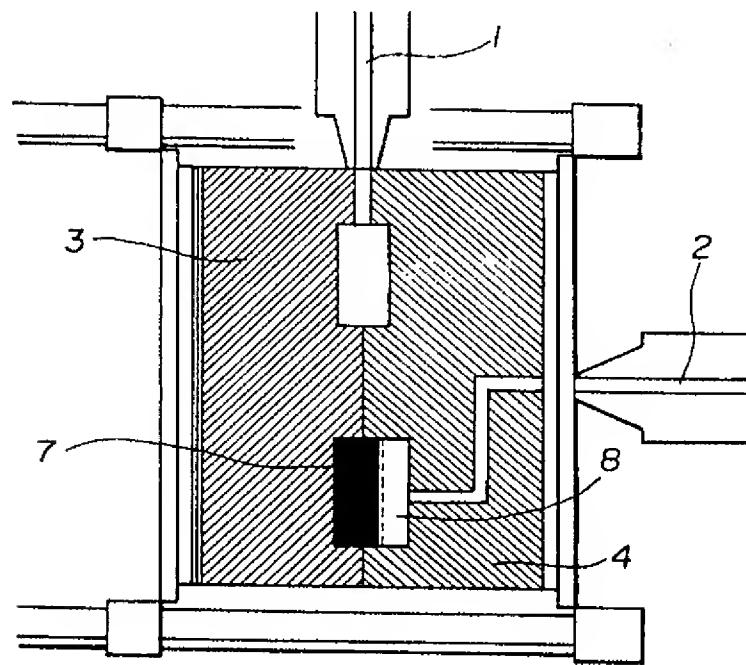


FIG.6

